### State of California California Environmental Protection Agency AIR RESOURCES BOARD

Draft

Protocol for Air Monitoring
Around a Structural Fumigation Application
of Sulfuryl Fluoride and Chloropicrin
Fall 2002

Prepared by
Operations Planning and Assessment Section
Quality Management Branch
Monitoring and Laboratory Division

Date: October 23, 2002

APPROVED:

Jeff Cook, Chief Quality Management Branch Ken Stroud, Chief Air Quality Surveillance Branch

Mike Poore, Chief Northern Laboratory Branch

Janette Brooks, Chief Air Quality Measures Branch Stationary Source Division

Bill Loscutoff, Chief Monitoring and Laboratory Division

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## Protocol for Air Monitoring Around a Structural Fumigation Application of Sulfuryl Fluoride and Chloropicrin Fall 2002

#### I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) (February 21, 2002 Memorandum, Sanders to Cook), the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticides sulfuryl fluoride and chloropicrin around a structural fumigation application, tentatively scheduled to be conducted in Fall 2002. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions...of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The product label for sulfuryl fluoride (Vikane®) requires that Chloropicrin be used as a warning agent during the fumigation. Monitoring will be conducted for both sulfuryl fluoride and chloropicrin around a single structural application. The study will be conducted around a fumigation for powderpost beetles, which requires an elevated level of fumigant relative to structural fumigation for other pests (e.g., termites).

The sampling and analysis will follow the draft procedures outlined in this protocol as well as the procedures described in Attachment I, "Standard Operating Procedure for the Determination of Sulfuryl Fluoride Measured as Fluoride by Ion Chromatography" and Attachment II, "Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector."

#### II. Sampling

Sulfuryl fluoride samples will be collected on charcoal sampling cartridges at a sample collection flow rate of 1 standard liters per minute (slpm). Two cartridges in series will be used for sample collection during the "mechanical aeration" sampling period. Only one sampling cartridge will be used for all other sampling periods.

Chloropicrin samples will be collected on XAD-4 resin sampling cartridges. For chloropicrin, the tubes are 8 mm x 140 mm, XAD-4, with 400 mg in the primary section, and 200 mg in the secondary section (SKC special order). Sample collection is at a flow rate of 90 standard cubic centimeters per minute (sccpm).

Subsequent to sampling, the tubes are capped, labeled, placed in a culture tube, and stored and transported in an insulated container with dry ice. The samples are transported (driven) to the ARB laboratory in Sacramento.

DPR recommends target 24-hour estimated quantitation limits (EQL) of 30 ug/m<sup>3</sup> and 0.1 ug/m<sup>3</sup> for sulfuryl fluoride and chloropicrin, respectively.

Caution should be used during field monitoring, transportation, storage, and lab analysis to minimize exposure of samples to sunlight in order to prevent photo degradation of chloropicrin.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, rotameter, train support, and a 12 volt DC vacuum pump (see Figure 1). Each tube is prepared in the field by breaking off each sealed glass end and then immediately inserting the tube into the fitting. The tubes are oriented in the sample train with a small arrow printed on the side of each tube indicating the direction of flow. Needle valves will be used to control the flow for sampling. The flow rates will be set using a calibrated digital mass flow meter (MFM) before the start of each sampling period. The MFM used for the chloropicrin samplers has a range of 0-100 sccpm and the MFM used for sulfuryl fluoride samplers has a range of 0-5 slpm. The MFMs have been calibrated to standard conditions (1 atm and 25 °C). The flow rate is also checked and recorded, using the MFM, at the end of each sampling period. Samplers will be leak checked prior to each sampling period with the sampling tubes installed. Any change in flow rates will be recorded in the field logbook (see Attachment IV). The pesticide sampling procedures for adsorbent tubes are included as Attachment III.

The fumigation process for powderpost beetles is expected to consist of a 36 to 72 hour exposure, a 1 to 4 hour mechanical vent period, followed by an 8 to 48 hour aeration period. The intention of this study is to target a fumigation using a shorter exposure period (i.e., 36 hours rather than 72 hours) as higher Vikane® application rates are required for the shorter exposure periods. The "mechanical vent" is conducted at the end of the exposure period, just prior to removal of the tarps. The purpose of the "mechanical venting" is to remove the gas between the tarp and the structure to minimize occupational exposure during removal of the tarps. For the purpose of this study, aeration is defined as starting when the tarps are completely removed. The aeration period required by the product label is a minimum of 8 hours. However, fumigation companies may choose to aerate the structure for a longer period of time. This study will target a fumigation using the label required 8 hour aeration period (i.e., reentry should be cleared after 8 hours of aeration). In either case the structure cannot be reentered until it is "cleared" as having Vikane® concentrations of less than 5 ppmv. The fumigator uses a Miran or Interscan gas analyzer to measure the Vikane concentration to clear the structure for reentry. The sampling schedule shown in Table 1 is intended as a guide. Exact sampling periods will be defined after the specific monitoring location is selected.

3

### Table 1 Fumigation Sampling Schedule

Sample period begins Sample duration time

Background (pre-application) 24 hours if possible; minimum 12 hours

(if <24 hours must meet 24-hour EQL)

Fumigation start Start of fumigation until 1 hour before

sunset

1 hour before sunset Overnight (until 1 hour after sunrise)

1 hour after sunrise Daytime (until 1 hour before sunset)

1 hour before sunset Overnight (until 1 hour after sunrise)

1 hour after sunrise Daytime (until mechanical aeration

begins)

Start of mechanical aeration Until the tarp is removed (about 1.5

hours)

Beginning of Aeration Until cleared (minimum 8 hours required

by label)

End of Aeration (when cleared)

Until 1 hour before sunset/ 1 hour after

sunrise

1 hour before sunset/ 1 hr after sunrise Daytime/Overnight

In addition, after completion of aeration (i.e., when the structure is cleared), two 24-hour samples will be taken at each of two different locations inside the fumigated structure (total of four samples).

The application monitoring study will be conducted at the location and under the conditions described in Table 2.

### Table 2 Application Information

Location:

To Be Determined (TBD)

Type of Structure:

TBD

Size of Structure:

**TBD** 

Product Applied:

Vikane®, chloropicrin

Type of Application:

Structural

Pest controlled:

Powderpost Beetle

Application Rate:

TBD (at "10x ounce hours")

Applicator:

TBD

Duration of Fumigation:

TBD (36 to 48 hours expected)

Duration of Vent

TBD (1 to 4 hours expected)

Duration of Aeration:

TBD (8 to 24 hours expected)

The structure selected for monitoring must have enough clearance surrounding it to allow for sampler placement at a distance of 5 and 10 feet from the edge of the structure. Per the DPR's request, 12 samplers will be placed surrounding the structure in 3 rings. The first ring consists of four samplers located at the middle of and 5 feet from each side of the structure. The second ring consists of four samplers 10 feet out from each corner of the structure. The third ring contains four samplers which would be placed 30 to 80 feet from each side or corner of the structure. A thirteenth sampler will be collocated with one sampler in the first ring and at the site expected to be downwind during aeration. The collocated sample will be collected at this site during each sampling interval. Sample inlets should be 1.5 to 2.0 meters above the ground. A fourteenth sampler will be used during the "mechanical aeration" stage and will be placed downwind of the structure (distance to be determined). Two more samplers will be placed inside the structure for collection of post-aeration samples. Background samples will be collected at the four corner (2<sup>nd</sup> ring) locations for 24 hours prior to the fumigation.

In regard to field data, the monitoring report will include:

- 1) An accurate record of the positions of the monitoring equipment with respect to the structure, including the exact direction and distance of the samplers from the edge of the structure:
- 2) An accurate record of pesticide application, including application time, method, dosage, fumigation duration, aeration method and duration;
- 3) An accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings and other obstacles with respect to true North.
- meteorological data collected at <u>1-minute</u> intervals including wind speed (mph) and direction, humidity, and air temperature and comments regarding degree of cloud cover, and
- 5) the elevation of each sampling station with respect to the structure, and the orientation of the field with respect to North (identified as either true or magnetic North).

#### III. Analysis

The draft sampling and analysis method and validation results for the sampling and analysis of sufuryl fluoride are included as Attachment II. The exposed charcoal sorbent tubes are frozen until desorbed with 10 milliliters (ml) of 40 millimolar (mM) sodium hydroxide (NaOH). An aliquot of the charcoal extract is evaporated to dryness and reconstituted to volume. Fluoride ion in the extract is separated by an anion exchange chromatographic method which employs an isocratic mobile phase and chemical suppression of background conductivity. The method detection limit (MDL) and estimated quantitation limit (EQL), expressed as fluoride, are 0.26 ug/sample and 1.3 ug/sample, respectively. For a 24-hour sample at 3.0 slpm, the MDL and EQL, expressed as sulfuryl fluoride, would be 0.16 ug/m³ and 0.80 ug/m³, respectively. The DPR target EQL was 30 ug/m³.

The draft sampling and analysis method and validation results for the sampling and analysis of chloropicrin are included as Attachment III. The chloropicrin method will consist of sampling with XAD-4 resin cartridges along with GC analysis with mass selective detector. The method detection limit (MDL) and estimated quantitation limit (EQL) for chloropicrin are 3.96 ng/sample and 19.8 ng/sample, respectively. For a 24-hour sample at 90 sccpm, the MDL and EQL would be 30.5 ng/m³ and 152 ng/m³, respectively. The DPR target EQL was 100 ng/m³. The analyses will be performed by the ARB laboratory in Sacramento.

#### IV. Field Quality Assurance

Field Quality Control for the structural monitoring will include the following:

- four field spikes will be obtained by sampling ambient air at the structural fumigation monitoring site for between 12 and 24 hours. The field spikes will be obtained by sampling ambient air during the background monitoring (i.e., collocated with a background sample at the same environmental and experimental conditions). The spike levels for sulfuryl fluoride and chloropicrin in the adsorbent tube samples have not yet been determined.
- 2) Four trip spikes will be prepared at the same level as the field spikes. The trip spikes will be labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.
- 3) Four lab spikes will be prepared at the same level as the field and trip spikes. The lab spikes will remain in the laboratory freezer and will be extracted and analyzed along with the field and trip spikes.
- 4) Collocated (replicate) samples will be taken for all sampling periods

(except the background period) at one sampling location (downwind).

5) A trip blank will be obtained, labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.

#### V. Personnel

ARB sampling personnel will consist of staff from the Air Quality Surveillance Branch of ARB.

#### VI. Safety Recommendations

Refer to Attachment V for general information on and toxicology of Vikane gas fumigant. The DPR's Monitoring Recommendations include the following safety recommendations.

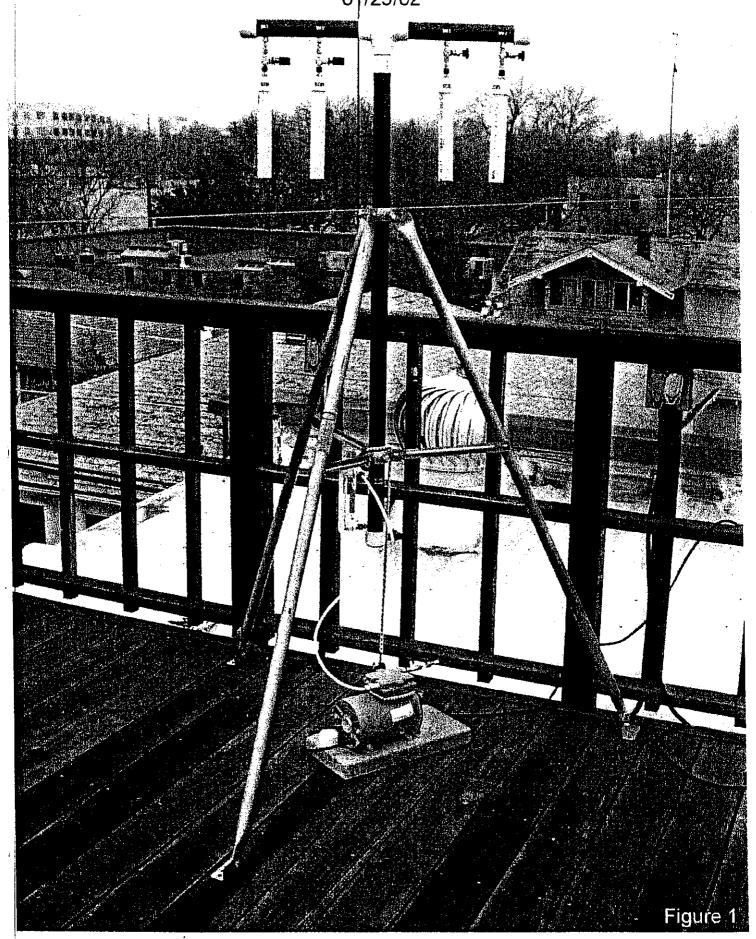
"Most of the following safety precautions pertain to applicators. In this recommendation, the sampling schedule is arranged to prevent sampling personnel from being near the structure during application. Therefore, most of these precautions are for reference only.

Product labels for the fumigants carry a danger warning. Inhalation of the vapors may be fatal or cause acute illness or delayed lung or nervous system injury if exposed to high concentrations. Do not get in eyes, on skin, or on clothing. Chloropicrin is also a strong lachrymator causing painful irritation to the nose and throat and causing tearing of the eyes. The labels recommend application personnel wear loose-fitting or well-ventilated long-sleeve shirt and long pants, and socks and shoes; chloropicrin also requires a full-face shield or safety glasses with brow and temple shields."

The highest ambient concentrations are expected during the 'mechanical vent' period. The DPR estimates, from tests conducted by the registrants, that the concentration of sulfuryl fluoride may be from 25,000 ug/m³ (6 ppmv) to 70,000 ug/m³ (17 ppmv) in the area surrounding the vent tube during the initial part of the mechanical vent period. However, the registrant tests showed that the ambient sulfuryl fluoride concentration decreased to below the monitoring detection limit of 0.006 ppmv at the start of aeration (e.g., after the tarp is removed). In order to insure the safety of sampling personnel, the "mechanical vent" period samples will be started just prior to turning on the "mechanical vent" fan. The "mechanical vent" sampling period for this study will end at the start of the aeration period (i.e., after tarp removal). Thus, sampling personnel will not be present during the mechanical vent period and so will not be exposed to the potentially higher levels present during that time.

Structures may be reoccupied when concentrations of sulfuryl fluoride are 5 ppmv or less.

### MANIFOLD SAMPLER 0 /29/02



#### Attachment I

Standard Operating Procedure for the Determination of Sulfuryl Fluoride Measured as Fluoride by Ion Chromatography



#### Air Resources Board



### Alan C. Lloyd, Ph.D. Chairman

1001 | Street • P.O. Box 2815 • Sacramento, California 95812 • www.arb.ca.gov

#### **MEMORANDUM**

TO:

Webster Tasat, Manager

Operations Planning and Assessment Section

FROM:

Russell Grace, Manager

Special Analysis Section

DATE:

July 23, 2002

SUBJECT:

DRAFT SOP FOR ANALYSIS OF SULFURYL FLUORIDE

The Special Analysis Section (SAS) will provide laboratory support for the sulfuryl fluoride pesticide monitoring program being conducted in 2002. The SAS laboratory has developed a draft standard operating procedure for the analysis of this compound, which SOP is attached. The method development data will be provided under a separate cover memo after the various quality assurance and quality control activities are completed.

If you have any questions, please contact Mr. Jim Omand of my staff at 324-1969 or me at 322-8959.

#### Attachment

cc: Dennis Goodenow Kevin Mongar T.E. Houston Jim Omand Michael Orbanosky

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Website: <a href="http://www.arb.ca.gov">http://www.arb.ca.gov</a>.

### California Environmental Protection Agency

### Air Resources Board

Special Analysis Section Northern Laboratory Branch Monitoring and Laboratory Division

#### **Preliminary Draft**

Standard Operating Procedure for the Determination of Sulfuryl Fluoride Measured as Fluoride by Ion Chromatography

July 23, 2002

Approved by:

Russell Grace, Manager Special Analysis Section

This SOP has been reviewed by staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.

#### 1. SCOPE

This document describes an ion chromatography (IC) procedure for the determination of sulfuryl fluoride, measured as fluoride (F-), from air samples collected on charcoal sorbent tubes. The Department of Pesticide Regulation (DPR) asked the Air Resources Board (ARB) to do application monitoring of sulfuryl fluoride at a requested quantitation limit of 30 micrograms per cubic meter ( $\mu g/m^3$ ).

#### 2. SUMMARY OF METHOD

Air samples are collected on charcoal sorbent tubes at a flow rate of one (1) liter per minute (lpm) over 24 hours. The exposed charcoal sorbent tubes are frozen until desorbed with 10 milliliters (ml) of 40 millimolar (mM) sodium hydroxide (NaOH). An aliquot of the charcoal extract is evaporated to dryness and reconstituted to volume. Fluoride ion in the extract is separated by an anion exchange chromatographic method which employs an isocratic mobile phase and chemical suppression of background conductivity.

#### 3. INTERFERENCES/LIMITATIONS

Method interference may be caused by contaminants in sorbent tubes, reagents, glassware or other processing apparatus that lead to discrete artifacts or elevated baselines. A method blank must accompany all quantitation runs to detect method interference

Matrix interference may be caused by ambient contaminants that extract from the sample. The extent of matrix interference may vary from source to source.

#### 4. EQUIPMENT AND CONDITIONS

#### A. INSTRUMENTATION

Ion Chromatograph: Dionex DX-500 Conductivity Detector: Dionex CD20

Pump, isocratic at 1.0 ml/min: Dionex GP 50 Chromatography Enclosure: Dionex LC20 Detector: Dionex CD20 Conductivity Detector

Printer: HP Laserjet 4100 PC: Dell OptiPlex G1

Column: Dionex AS14 Ion Pac 4x250 mm Guard column: Dionex AG14 Ion Pac 4x50 mm

Supressor: Dionex ASRS-Ultra 4 mm

#### Auto Sampler:

Vial type – 0.5 ml Setup - injection type = loop, 25 µl Injection mode = proportional Bleed = off ini/vial = 1

#### В. **AUXILIARY APPARATUS:**

- 1. Desorption vials, VWR 20 ml with teflon screw caps.
- 2. Sampler vials, Dionex 0.5 ml.
- 3. Syringe, Gastight.
- 4. Syringe filter units, Whatman 1.0μm PTFE.
- 5. Disposable syringes, 3 ml.
- 6. Hot plate, Corning PC-420

#### Sonicator, Branson 1200 lla C.

- 10 N NaOH, reagent grade.
- 2. IC mobile phase and sample desorbant,40 mM NaOH, 8 ml 10 N NaOH dilute to water with deionized water.
- Sorbent tubes, SKC coconut charge all type B(SKC 226-09).
   Fluoride standard, Dipriex 1000 /- 14 mg/L in deionized water.
- 5. Sulfuryl fluoride gas standard, 38.0 ppm +/- 2%, Scott-Marrin.

#### 5. ANALYSIS OF SAMPLES

- 5.1 The field samples are collected on charcoal sorbent tubes which are stored in a freezer after exposure and before desorption.
- 5.2 Remove the glass wool plug from the primary end of the charcoal tube with forceps. Pour the primary resin bed into a 20 ml desorbing vial and add 10 ml of 40 mM NaOH to the vial. Cap the vial tightly. Retain the secondary section of the charcoal tube resin bed for later analyses.
- 5.3 Place the desorbing vial into the sonicator for 1 hour. Filter the NaOH extract through a 1.0 µm syringe filter. Put 5 ml of the extract into a clean 20 ml desorption vial. Place the uncapped extract vial on a hotplate and evaporate to dryness.
- 5.4 Remove the vial from the hot plate and allow to cool. Reconstitute the vial with 5 ml of deionized water and mix the vial contents thoroughly. The contents of the vial is now ready for IC analysis.

- 5.5 Establish HPLC operating parameters by using Chromeleon software. From the Browser screen select the equilibrate icon and monitor the detector signal. When baseline is stable the IC is ready for analysis.
- 5.6 Create an analysis worklist which contains the following elements: a set of six calibration standards, a reagent blank, a charcoal resin extraction blank, a lower calibration range charcoal gas spike and a high calibration range charcoal gas spike. A calibration check sample should be analyzed after each group of ten field samples and at the end of the analysis batch. When creating a worklist use file name SO2F2a for the worklist program and fluoride for the worklist method file.
  - 5.7 The autosampler is setup by pouring 0.5 ml of sample into 0.5 ml sample vials and loading the vials into sample carriers in the same order as the sample schedule. Autosampler parameters are not set automatically when the method is loaded, so they must be checked before a sample run is started.
  - 5.8 A sample batch can be submitted for analysis from the browser software by clicking on the batch start icon.
  - 5.9 Method calibration is automatically updated by designating calibrators on the worklist. Atmospheric concentration is calculated according to:

Conc., μg/m<sup>3</sup> = (Amount, μg/m × 10.0 ml) Air Volume Sampled, m<sup>3</sup>

#### 6. QUALITY ASSURANCE

#### A. INSTRUMENT REPRODUCIBILITY

Five injections of standards at three concentrations are made in order to establish the reproducibility of the instrument. The concentrations used should be at the high, middle and low areas of the calibration range.

#### B. CALIBRATION

A calibration curve is determined by linear regression analysis of six calibration standards. The correlation coefficient for the linear regression must be 0.995 or greater.

#### C. CALIBRATION CHECK

A calibration check sample is run after every tenth field sample to verify system calibration. Calibration check samples must be within 10% of the assigned

value. If the check sample is out of range then the affected samples must be reanalyzed.

#### D. MINIMUM DETECTION LIMIT

Detection Limit is based on USEPA MDL calculation. Using the analysis of seven replicates of a low level matrix spikes, the method detection limit (MDL), and the estimated quantitation limit (EQL) for fluoride were calculated by:

$$MDL = 3.14*s$$

$$EQL = 5*MDL$$

where: s = the standard deviation of the concentration calculated for the seven replicate spikes. Given s = 0.0084 ng/ml for the seven samples, the MDL and EQL of fluoride are calculated as follows.

Based on the 10.0 ml extraction volume and assuming a sample volume of 0.144 m<sup>3</sup> (1.0 lpm for 24 hours) the MDL and EQL for ambient concentration of fluoride are:

MDL = 
$$(0.026 \mu g / ml) (10 ml) / 0.144 m3 = 1.8 \mu g / m3 fluoride$$

EQL= 5 (1.8 
$$\mu$$
g / m<sup>3</sup>) = 9.0  $\mu$ g / m<sup>3</sup> fluoride

The equivalent MDL and EQL expressed as sulfury! fluoride for a 24 hour sample are:

MDL = 
$$(1.8 \mu g / m^3) (102/38) = 4.8 \mu g / m^3$$
 sulfuryl fluoride

EQL = 
$$(9.0 \mu g / m^3) (102/38) = 24 \mu g / m^3$$
 sulfuryl fluoride

#### E. EXTRACTION EFFICIENCY

Extraction efficiency is established by extracting and analyzing spiked sorbent tubes that are not exposed to field sampling conditions. Three replicates at two levels are extracted with the average and standard deviation determined for the replicates. The average amount divided by the amount added multiplied by 100 gives the percent recovery.

#### F. COLLECTION EFFICIENCY

Collection efficiency is established by extracting and analyzing spiked sorbent tubes that have been exposed to field sampling conditions. Three replicates at two levels are extracted with the average and standard deviation determined for the replicates. The average amount divided by the amount added multiplied by 100 gives the percent recovery.

#### G. STORAGE STABILITY

A storage stability study is conducted over an eight week period. Tubes are spiked with sulfuryl fluoride gas at low and high calibration levels. The spiked tubes are stored in the freezer at -20°C and extracted/analyzed at spaced time intervals.

#### H. BEREAKTHROUGH

The primary resinfect of three charcoaltesin tubes are each spiked with a high level of sulfuryl fluoride. The resin tubes are placed in a sampler and exposed to field sampling conditions (1.0 lpm) for 24 hrs. The tubes are removed from the sampler and both primary and secondary resin beds are analyzed for sulfuryl fluoride. The analytical results are evaluated for spike recovery in the primary bed and the presence of sulfuryl fluoride in the secondary bed.

#### 7. SAFETY

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. Therefore, each chemical compound must be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level. Material safety data sheets (MSDS's) should be on file for all analytes and reagents.



#### Air Resources Board

### Gray Davis Governor

### Alan C. Lloyd, Ph.D. Chairman

1001 | Street • P.O. Box 2815 • Sacramento, California 95812 • www.arb.ca.gov

#### **MEMORANDUM**

TO:

Webster Tasat, Manager

Operations Planning and Assessment Section

FROM:

Russell Grace, Manager

Special Analysis Section

DATE:

July 24, 2002

SUBJECT:

METHOD VALIDATION DATA FOR ANALYSIS OF SULFURYL

**FLUORIDE** 

The Special Analysis Section provides laboratory support for the pesticide air monitoring program implemented by the ARB at the request of the Department of Pesticide Regulation. One of the responsibilities of the SAS is laboratory analytical method development. By way of this memo, we are providing you with the method validation data generated in the development of the sulfuryl fluoride analytical method for the 2002 monitoring season. The attached tables contain the currently available data generated to determine the method detection limit (MDL), estimated quantitation limit (EQL), reproducibility, extraction efficiency, collection efficiency, storage stability and breakthrough.

All of the method development procedures were summarized in the draft standard operating procedure (SOP) for sulfuryl fluoride. This draft SOP was previously provided to you.

If you have any questions, please contact Mr. Jim Omand at 324-1969 or me at 322-0223.

#### Attachment

cc: Michael Poore T. E. Houston Jim Omand Kevin Mongar

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Website: <a href="http://www.arb.ca.gov">http://www.arb.ca.gov</a>.

TABLE 1

METHOD DETECTION LIMIT fluoride

HUOLIC	10 <u> </u>
	μg/ml
1	0.273
. 2	0.251
3	0.254
4	0.256
5	0.246
6	0.255
7	0.254
Average	0.256
Standard Deviation	0.00838
MDL (3.14*sd)	0.026
EQL	0.13

TABLE 2
REPRODUCIBILITY STUDY

sulfuryl fluoride (μg/ml)

#	Low Level	Med Level	High Level	
1	0.273	0.884	2.315	
2	0.251	1.091	2.394	
3	0.254	1.099	2.365	
4	0.256	1.094	2.335	
. 5	0.246	1.115	2.424	
Average	0.256	1.06	2.37	
Std. Deviation	0.01	0.1	0.044	
Coef. Variation	3.90%	9.20%	1.90%	

TABLE 3
EXTRACTION EFFICIENCY

	7.66 μg spike	20.4 μg spike
	7.38	19.7
	8.13	20.0
	8.09	21.0
Average	7.87	20.2
Std. Deviation	0.42	0.69
recovery	103 %	99 %

TABLE 4
COLLECTION EFFICIENCY

	2.55 μg spike	7.66 μg spike
	1.83	7.91
	2.45	6.73
	2.10	6.88
Average	2.13	7.17
Std. Deviation	0.31	0.64
recovery	84 %	94%

TABLE 5
STORAGE STABILITY

Storage Time	7,6	66 μg	20.	<b>4</b> μg
	μg	% recovery	μg	% recovery
1 day	8.01	105	21.07	103
10 days	7.66	100	19.36	95
19 days	7.85	102	19.02	93
49 days	7.38	96	19.68	96
55 days	8.20	107	22.00	108

TABLE 6
BREAKTHROUGH

137 μg	Primary Bed (μg)	Secondary Bed (µg)		
1	133	0.6		
2	134	0.5		
3	143	0.7		
Average	137			
Std. Dev.	5.5			
recovery	100%			

#### Coconut Charcoal Breakthrough Study Sulfuryl Fluoride 3 liters per minute

Duration (hours)	Primary Bed (ug)	Percent Recovery	Average	Stdev
3 (137ug)	133.4	97.37		
	122.5	89.42	93.3942	5.6259
12 (137ug)	123.2	89.93		
	132.5	96.72	93.3212	4.8001
24 (137ug)	131.7	96.13		
	135.0	98.54	97.3358	1.7032
LCS (137ug)*	141.5	103.3		
	142.6	104.1	103.6861	0.5677

Duration	Secondary Bed	Percent		
(hours)	(ug)	Recovery	Average	Stdev
3 (137ug)	1.7500	1.28		
·	1.9430	1.42	1.3478	0.0996
12 (137ug)	3.6370	2.65		
L	1.1220	0.82	1.7369	1.2981
24 (137ug)	2.1500	1.57		
	1.4120	1.03	1.3000	0.3809
LCS (137ug)*	3.2210	2.35		
	2.9500	2.15	2.2522	0.1399

#### Notes:

Samples were not subject to 3 lpm flows Micrograms

ug

Standard deviation Stdev

#### Attachment II

Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector

### California Environmental Protection Agency

### Air Resources Board

Standard Operating Procedure
Sampling and Analysis of Trichloronitromethane
(Chloropicrin) in Application and Ambient Air
using Gas Chromatography/Mass Selective
Detector

Special Analysis Section Northern Laboratory Branch Monitoring and Laboratory Division

06/25/01 version

Approved by:

Russell Grace, Manager Special Analysis Section

#### SCOPE

The current method is for the analysis of trichloronitromethane (TCNM) using a gas chromatograph/mass selective detector. The procedure is for the analysis of application and ambient air monitoring of TCNM using XAD-4 resin tubes. The Department of Pesticide Regulation (DPR) asked the Air Resources Board (ARB) to analyze for TCNM during agricultural/structural application with a requested quantitation limit of 1.0 µg/m<sup>3</sup> and ambient monitoring with a quantitation limit of 0.1 μg/m<sup>3</sup>.

#### SUMMARY OF METHOD

Resin tubes, XAD-4, are placed on the sampler for 24 hours at a flowrate of 0.1 liters per minute (LPM or 100 mLPM). The samples are stored in an ice chest or refrigerator until extracted with 3 ml of dichloromethane (DCM). The injection volume is 1 μl. A gas chromatograph with a mass selective detector in the selected ion monitoring (SIM) mode is used for analysis.

#### 3. INTERFERENCES/LIMITATIONS

Interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. A method blank, including both solvent and resin, must be analyzed with each batch of samples to detect any possible interferences.

#### 4. **EQUIPMENT AND CONDITIONS**

#### A. Instrumentation:

Hewlett-Packard 6890 Series gas chromatograph Hewlett-Packard 5973 Network mass selective detector Hewlett-Packard 6890 Enhanced Parameters ALS

MS Transfer line: 280°C

Injector: 210°C, Splitless, Liner 4 mm straight liner with glass wool. Column; Restek Rtx-200, 60 meter, 320 µm i.d., 1.5 µm film thickness.

GC Temperature Program: Oven initial 40°C, hold 4 min. Ramp to 220°C

12°C/min., hold 1 min., ramp to 240°C @ 20°C/min., hold 2.0 min.

Retention time: TCNM 11.93 min.

Splitter open @ 1.0 min.

Flows: Column: He, 1.6 ml/min, 9.1psi. (velocity: 32cm/sec)

Splitter: 50 ml/min.

24

Mass Spectrometer: Electron Ionization Selective Ion Monitoring: trichloronitromethane: 117 (quant. ion 100%), 119 (qual. ion 98%); Tuning: PFTBA on masses 69, 219, 502.

#### B. Auxiliary Apparatus

- 1 Precleaned vials, 8 ml capacity with teflon caps.
- 2 Whatman filters, 0.45 μm
- 3 Disposable syringes, 3 mi
- 4 Sonicator
- 5 GC vials with septum caps.

#### C. Reagants

- 1 Dichloromethane, Pesticide grade or better.
- 2 Trichloronitromethane, Chem Service PS-4, 98.8%
- 3 XAD-4 resin sorbent tubes, 400/200mg. SKC, Fullerton, CA.

#### 5. ANALYSIS OF SAMPLES

- A daily manual tune shall be performed using PFTBA. The instrument is tuned using masses: 69, 219, 502. The criterion for the tune are the peak widths at  $\frac{1}{2}$  the peak height, 0.60  $\pm$  0.05, and the criteria for relative abundance; 69:100%, 219:100-120%, and 502: 7-12%.
- 2 It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample which may result in possible carry-over contamination.
- 3 A 5-point calibration curve shall be analyzed with each batch of samples. For the ambient studies the calibration will be 0.5-50.0 ng/mL and for the application studies 50.0-500 ng/mL.
- 4 A calibration check sample of 7.5 ng/ml is run after the calibration and every 10 samples and at the end of the sample batch. The value of the calibration check must be within ±3σ (the standard deviation) or ±10% of the expected value whichever is greater. If the calibration check is outside this limit, then those samples in the batch after the last calibration check that was within limits need to be reanalyzed.
- With each batch of samples analyzed, a laboratory blank and a laboratory control spike will be run concurrently. A laboratory blank is XAD-4 extracted and analyzed the same way as the samples. A laboratory control spike is XAD-4 spiked with a known amount of

standard. The laboratory control sample is extracted and analyzed the same way as the samples. Laboratory control samples should have recoveries that are greater than or equal to 70% of the theoretical spiked value.

- 6 Score and snap the sample resin tube, transfer the front bed of the resin tube into a 8 ml vial. (Save the back-up bed for future analysis if necessary.) Rinse the tube with 3.0 ml of DCM into the extraction vial. Cap and place the vial in the sonicator for 1 hour.
- 7 Filter the samples using 0.45 μm filter attached to a 3 ml syringe directly into a GC vial and cap securely.
- 8 The atmospheric concentration is calculated according to:

Conc (ng/m³) = Extract Conc (ng/ml) X 3 ml / Air Volume Sampled (m³)

#### 6. QUALITY ASSURANCE

#### A. Instrument Reproducibility

The reproducibility of the instrument and analytical method was established by analyzing five (5) 1.0 µl injections of trichloronitromethane standard at three concentrations (low, mid, and high). The low, mid and high concentrations were 5, 20 and 50 ng/ml, respectively.

#### B. Calibration

A five-point calibration curve is made ranging from 5.0 ng/ml to 50.0 ng/ml for ambient and 50 ng/ml to 500 ng/ml for application.

#### C. Calibration Check

A calibration check sample is run after the calibration, after every 10 samples and at the end of the sample batch to verify the system is in calibration. The value of the check must be within  $\pm 3\sigma$  (the standard deviation) or  $\pm 10\%$  of the expected value whichever is larger. If the calibration check is outside the limit, then those samples in the batch after the last calibration check that was within the limit need to be reanalyzed.

#### D. Minimum Detection Limit

The detection limit is based on US EPA MDL calculation. Using the analysis of seven (7) replicates of a low-level matrix spike, the method detection limit (MDL) and the estimated quantitation limit (EQL) for trichloronitromethane is calculated by: MDL = 3.14\*(std dev values) where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. For TCNM the MDL is 3.96 ng/sample (1.32 ng/mL). EQL, defined as 5\*MDL, is 19.8 ng/sample (6.60 ng/mL) based on a 3 ml extraction volume. Results are reported to 3 significant figures. Results below EQL but above the MDL are reported as DET (detected) and results less than the MDL are reported as ND (nondetect).

#### E. Collection and Extraction Efficiency (Recovery)

Trichloronitromethane at a low and high level are spiked on XAD-4 tubes (3 at each concentration). The spiked tubes are placed on field samplers with airflows of 100 mLpm for 24 hours. The samples are extracted with DCM and prepared as described in section 5, #6-7. The average percent recovery of trichloronitromethane should be ± 20% of the expected value. The recoveries both for the low and high levels are greater than 80.0%.

#### F. Storage Stability

Storage stability was set up for a 4-week study. Three (3) XAD-4 tubes each were spiked at the low and high-end concentrations. The tubes were stored in the freezer until analyzed. At the low-end concentrations (5 ng/ml), the recovery for the three spikes averaged 106.8 percent, ranging from 103.68 to 113.68 percent. The average percent recovery peaked after fourteen days and was at the lowest after 28 days. At the high end (50 ng/ml), the recovery for the three spikes averaged 90.237 percent, ranging from 88.904 to 91.996 percent. The average percent recovery peaked at 14 days and was at the lowest at 20 days.

#### H. Breakthrough

The previous analysis of trichloronitromethane (ARB #A5-169-43) was for 4 hour sampling at 1.0 LPM in September/October, 1986. The current study for ambient monitoring for 24 hours will require a low sample flow rate to meet the requested EQL. A breakthrough analysis study was conducted. The flow rates tested were 1.0, 0.5, 0.2 and 0.1 Lpm. To meet the EQL and minimize breakthrough possibility, the flow rate for the field sampling will be at 100 mLpm.

#### H. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

55

#### Attachment III

### Application Sampling Procedures For Adsorbent Tubes

### Application Sampling Procedures For Adsorbent Tubes

#### Overview:

- Collect samples, according to the schedule in Table 1 of this protocol.
- Collect 4 background samples, from each corner sampling position.
- -Collocate 1 field spike with each of the 4 background samples.
- -Collect a collocated sample from the downwind site for all sampling periods (except the background period).
- -Submit 1 trip blank.
- -With the trip blank there should be a total of 126 samples collected during the study, plus 4 trip and 4 field spikes (for each chemical, sulfuryl fluoride and chloropicrin).
- --All samples are stored either in an ice-chest on dry ice or in a freezer.
- The field log sheet is filled out as the sampling is conducted. All QA samples must be logged onto the log sheet.
- The chain of custody (COC) forms are filled out prior to sample transfer; the originals are transferred with the samples; make and retain copies if desired (not necessary).

#### Sampling Procedure:

Materials that will be needed to conduct the sampling include:

- -Clip board with log sheets
- -pencils/pens
- -sample labels
- -sample cartridges
- -end caps
- -plastic test tubes
- -zip-lock bags
- -0 to 100 sccpm mass flow meter (MFM) with battery
- -ice chest
- -dry ice

Figure out the route for sampling the 8 locations and try to keep this the same throughout the study.

#### Preparation and Set-up

On the way to study site, plug the MFM into the battery. It takes the MFMs about 10 minutes to warm up before they can be used. Leave the MFM plugged in until the last sample is taken; unplug when not in use to minimize drop in battery charge. Recharge

the batteries once per week to be on the safe side.

Securely attach one adsorbent sample cartridge to the sampling tree. MAKE SURE THE ARROW ON THE CARTRIDGE IS POINTING TOWARDS THE SAMPLE LINE.

Set the sampler to the correct flow rate. Perform the leak check on each sample line by placing a plastic tube cap over the inlet of the cartridge (with the pump on). The rotameter ball should fall to zero. The leak check should be performed before setting the flows with the MFMs.

Using the MFM set the flow rate exactly the specified flow rate.

Make sure that the rain/sun cover is pulled down over the sample tube.

Fill out the log sheet, including: log #, start date, time, start counter reading, leak check OK, MFM Serial #, any comments and the weather conditions.

#### Sample collection and Shipment

Measure (do not re-set) the flow rates at the end of the sampling period with the MFM; leak check the sample lines; record the end data on the log sheet.

Remove the sample cartridge and cap the ends. Attach the sample label like a flag on the secondary end of the tube. Make sure that the label does not cover the glass wool separating the primary and secondary beds in the cartridge.

Place the cartridge in the plastic test tube shipping container.

Place all the samples for each period in a zip-lock freezer storage bag and place on <u>dry</u> <u>ice</u> in a cooler.

Collect a trip blank (TB) by breaking the ends off of a tube, capping and labeling as usual and storing along with the rest of the samples. Log the TB into the log sheet.

Attachment IV
Field Log Sheet

#### **CARTRIDGE FIELD LOG SHEET**

Project: Chloropicrin Fumigation Air Monitoring Study

Project #: P-02-004 On Flow: 90cc +/-1.0cc Off Flow: 90cc +/-10%

Log	Sample	Sampler		Time	Counter	Flow	True	Comments	Weather	
#	Name	J ID	On	On	On	On	Flow		K,P,C,F&R	
		Number	Off	Off	Off	Off			On	Off
				I						
								·		
				,						
			_							
				<u> </u>				•	·	
				ļ						
				•						
i		}								
				ļ						
		1								
									ļ	
ł				ļ					ļ	<del></del>
				<del> </del>					<del>                                     </del>	
		[ }								
i		}								
	***		**	1						
		<u> </u>			-					
<del></del>			- ··· · ··· - · · · · · · · · · · ·	<del> </del>		•				
										<del></del>
		<u> </u>								
			···							
		<u> </u>						İ		
$\overline{}$										
			- July - Liny							
+									-+	
j		-						· •		
6/1	M Used #:		Slope:	·i	Intercept:	1				

of 6

#### **CARTRIDGE FIELD LOG SHEET**

Project: Sulfuryl Fluoride Fumigation Air Monitoring Study
Project #: P-02-004 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

Log	Sample	Sampler	Date	Time	Counter	Flow	True	Comments	Weather	
#	Name	ID	On	On	On	On	Flow		K,P,C,F&R	
		Number	Off	Off	Off	Off			Off	Off
										<u> </u>
								·		<del> </del>
			<del>-</del> .							-
	- t., //-			<del>_</del> -						
									·	
i										
								· · · · · · · · · · · · · · · · · · ·		
	٠	]								
		-								
		}				i				_
		1								
1										
	-									
				·						
		<b> </b>		<del></del>						
	<u> </u>									
		-						<b> </b>		
			*							
								·		
								_		
			····	-						
]								ŀ		
		1								
		<u> </u>	15.44**					<b>†</b>		
M	FM Used #:		Slope:		Intercept:	•				

ယ္

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog, and R = Rain (any)

#### Attachment V

General Information On Vikane Gas Fumigant

# 

#### INTRODUCTION

Drywood termites and other wooddestroving insects can cause significant damage as they feed on materials containing cellulose found in structures, such as wood, paper, textiles, furnishings, and works of art. Because these insects live most of their life cycle within their food source, the exact distribution and extent of infestation is often difficult to determine. Therefore, localized treatments using physical methods or conventional insecticides may not eradicate all wood-destroying insects infesting a structure. To solve this problem The Dow Chemical Company developed sulfuryl fluoride, the active ingredient of Vikane\* gas fumigant, to be used exclusively by professional fumigators (DowElanco 1992).

Research conducted during the development of sulfuryl fluoride demonstrated that this fumigant possesses highly desirable characteristics for the eradication of structure-infesting insects (Derrick et al. 1990). Sulfuryl fluoride is nonflammable, non-corrosive, and does not cause undesirable odors. It quickly penetrates structural materials, is effective against a variety of structural pests, and dissipates rapidly during aeration (Kenaga 1957; Stewart 1957). Since first marketed as Vikane in 1961. sulfuryl fluoride has been used to fumigate more than one million buildings, including museums: historical landmarks, such as the Hearst Castle in California (Pest Control 1977) and the Flagier Museum in Florida (Moon 1981), rare book libraries, government archives, scientific and medical research laboratories, and food-handling facilities.

#### **EFFICACY**

Vikane has been demonstrated to reduce oxygen uptake in insect eggs (Outram 1970). Vikane also prevents insects from metabolizing the stored fats they need to maintain a sufficient source of energy for survival by disrupting the glycolysis cycle (Meikle et al. 1963). This metabolic imbalance may delay mortality of insects for several days or more following fumigation (Osbrink et al. 1987). For this reason, insects that have received a lethal exposure to Vikane may still be alive immediately following fumigation.

The activity of Vikane depends on the concentration reaching the target pest and the duration of exposure. Therefore, the dosage of Vikane required for a specific target pest is calculated in "ounce-hours," ounces of Vikane multiplied by hours of exposure. Insect eggs require a higher ounce-hour dosage of Vikane compared to later life stages. Control of the egg stage of social insects, such as termites and ants, is not necessary because newly hatched termites and ants cannot survive without adult care.

Higher dosages required to control eggs of insects, such as wood-boring beetles, can be obtained by increasing the exposure time, increasing the concentration of Vikane, or a combination of both. Fumigators use the Fumiguide\* calculation system, which was developed specifically for Vikane, to determine the amount of Vikane required for specific pests and fumigation conditions.

Vikane has also been successfully used since 1961 to control a wide variety of household pests, including cockroaches, clothes moths, rodents, bedbugs and carpet beetles. The eradication of eggs of carpet beetles requires very high dosages of Vikane (Su and Scheffrahn 1990) which are not economically practical. Therefore, two fumigations are required to eradicate carpet beetles using Vikane. The second fumigation is conducted after all beetle larvae have hatched from eggs surviving the first fumigation.

-

### FORMULATION AND PROPERTIES

Sulfuryl fluoride, the active ingredient of Vikane, is a gas at temperatures above -67°F. Vikane is packaged in white cylinders as a liquid under pressure, containing 99.5% sulfuryl fluoride with no other pesticides, solvents or additives. Vikane has a high vapor pressure; it evaporates 20,000 times more readily than mothballs and therefore disperses rapidly from structures.

Vikane does not react with common household furnishings. This is why fumigation with Vikane is an established method used to eradicate pests infesting delicate and rare biological and historical museum artifacts. Food must be protected from exposure to Vikane during fumigation because no residue tolerances have been set for any food product (see PREPARATION). Vikane does not form toxic surface residues in household items, and thus dishes, clothes, and other items do not need to be washed following fumigation with Vikane.

Watering soil around exterior perimeter building foundations is recommended to reduce both loss of fumigant through the soil and exposure of plant roots to Vikane during fumigation. The solubility of sulfuryl fluoride in water is very low, 0.075% by weight at 77°F (Meikle and Stewart 1962).

Vikane is nonflammable and relatively stable; however, it will react to form hydrogen fluoride at extremely high temperatures exceeding 752°F. This acid can etch metals, glass, ceramic tille, or china near the heat source. Thus, prior to structural fumigation, all open flames and glowing heat filaments are turned off or disconnected.

Vikane is odorless at concentrations used to fumigate structures and is not irritating as a gas to the eyes or skin. For these reasons, a trace amount of the warning agent, chloropicrin, is introduced in the structure prior to fumigation to warn people and animals that the structure is being fumigated. Chloropicrin acts as a warning by causing irritation of the eyes, tears, discomfort, and has a noticeable disagreeable pungent odor even at very low concentrations, less than 1 part per million (ppm).

Chloropicrin diffuses from structures more slowly than Vikane. Thus, occupants may experience some eye irritation after all of the Vikane has aerated from the structure. The furnigator should be contacted to take remedial measures if this occurs. A trained fumigator will use an approved clearance device, such as an Interscan<sup>1</sup> or Miran<sup>2</sup>, to determine that the concentration of Vikane within the structure is 5 ppm or less prior to allowing anyone to reoccupy the structure.

### FUMIGATION PREPARATION

The label for Vikane requires that the following preparations be completed prior to releasing the furnigant into the structure.

- All animals (including fish) and plants must be removed from the structure to be fumigated.
- Mattresses and pillows completely enveloped in water-proof covers (not including waterbeds) must be removed from the area to be fumigated if the covers can not be removed. The water-proof covers restrict dispersion of fumigant during aeration.
- All flames such as pilot lights and electric heating elements must be turned off for reasons previously described<sup>3</sup>.
- 4. The following should be opened prior to furnigation: internal doors, internal openings to attics and sub-areas, storage chests, cabinets, drawers, closets, and appliances such as washers, dryers and ovens. In tarpaulin furnigations, operable windows are opened. These procedures assist in rapid dispersion of Vikane during furnigation and aeration.
- Food, feed, drugs and medicinals, including items in refrigerators and freezers, must be removed from the fumigation site or sealed in highly resistant containers such as glass, metal or plastic or enclosed in special bags according to label directions.

This is required because exposure of unprotected foodstuffs to Vikane may result in the formation of temporary sulfuryl fluoride residues and permanent fluoride residues. However, experimental exposure of food commodities protected in two nylon bags to 10x dosages of Vikane resulted in no detectable sulfuryl fluoride or added fluoride residues. Two nylon bags reduced the exposure of protected foodstuffs to Vikane by 99.99% (Scheffrahn et al. 1990). Excessive exposure to fluoride can have toxicologically significant effects, although longterm human intake of water containing up to 1 mg/l (1 ppm) fluoride is generally considered not to result in adverse effects. (National Research Council 1977).

#### FUMIGANT DOSAGE DETERMINATION

Because of a multitude of structural, environmental, and fumigation variations. there are no two fumigation jobs that are identical. The required dosage of Vikane is influenced by the temperature at the site of the pest, the length of the exposure period and the susceptibility of the pest to be controlled. Consequently, the dosages vary, but the typical single family home fumigation involves the use of 6-16 ounces/1000 cubic ft (1440-3850 ppm). The length of the exposure period is critical to accumulate sufficient ounce-hours4 required for the temperature at the site of the pest. The ounce-hours required to control target insect pests have been determined from laboratory and field test-

#### RELEASING VIKANE

Five to ten minutes prior to introducing Vikane into the structure, the fumigator will place a warning agent, chloropicrin, in the structure. This warning agent is required to warn any person or animal that may have entered the structure after the final inspection by the fumigator. Once the building is determined to be cleared of all people and animals, the fumigator will release the Vikane into the structure.

Vikane is packaged in 125 lb. cylinders that fumigators transport on their vehicles. The fumigator introduces Vikane through tubing into the air stream of a fan that helps disperse the fumigant throughout the structure. Once the appropriate amount of Vikane is introduced, the fumigator turns off the cylinder valve and removes the tubing from the cylinder.

### FUMIGATION PERIOD

Vikane is usually held in the structure for approximately 16-30 hours. Fumigation time is dependent upon the factors mentioned previously<sup>5</sup>. When the fumigation exposure period is complete, the fumigator will return to the structure to conduct the aeration procedure.

#### **AERATION**

Aeration is the final step of a fumigation. Aeration involves proper ventilation and clearance of Vikane and the warning agent, chloropicrin, from a structure.

The Occupational, Safety & Health Administration (OSHA) established a Permissible Exposure Level (PEL) of 5 parts per million (ppm) for Vikane. A PEL is the Time Weighted Average (TWA) exposure to which it is believed that most members of a healthy working population can be exposed 40 hours/week for a working lifetime.

The fumigator must aerate a structure so that the concentration of Vikane in the air is 5 ppm or less prior to allowing reentry. This 5 ppm PEL is substantially lower than the level that may affect people and pets following even long-term exposure.

Unlike liquid and solid insecticides, Vikane is a gas possessing a very high vapor pressure (potential to escape from an area) and low boiling point (it is a gas above -67°F). During aeration of the fumigated structure, Vikane will quickly diffuse from high concentrations within a structure to the outside air where it rapidly dissipates to nondetectable levels.

Degassing is the process of fumigant diffusing out of materials when the concentration of gas is less around the object than within the object. Required aeration procedures allow the fumigant time to diffuse from structural voids and household materials and be ventilated out of the structure. The fumigator will use powerful fans and open cabinets, doors, and windows to speed the process of aeration.

Many structures have been tested by university researchers and DowElanco'scientists with the goal of developing new aeration procedures. The aeration procedures have been vigorously tested to ensure that even under poor ventilation conditions concentrations of Vikane will not increase after occupants return.

Only specially trained and statelicensed/certified professionals can determine that a structure can be reoccupied. Unique equipment, such as the Interscan and Miran, must be used to test the concentrations of Vikane within structures. The Interscan is specially designed to detect levels of Vikane down to 1 ppm.

### VIKANE AND THE ENVIRONMENT

When Vikane is aerated from a structure it rapidly dissipates into the atmosphere because of its high vapor pressure. Vikane is broken down mainly through hydrolysis to release fluoride and fluorosulphate ions. Ultraviolet radiation and reactions with solid particles in the atmosphere may also catalyze the breakdown of Vikane.

The relatively small amounts of Vikane released are calculated to have virtually no impact on global atmosphere/environment. Sulfuryl fluoride is fully oxidized, and thus is not expected to interact or contribute to local ozone formation (such as Los Angeles smog) because of its low reactivity in the atmosphere. The relative contribution of Vikane to acid rain is infinitely small compared to the massive amount of sulfur released into the atmosphere from industry. Vikane contains no chlorine or bromine and thus can not react to deplete stratospheric ozone by the known mechanisms (Bailey 1992).

### TOXICOLOGY OF VIKANE

#### Mode of Action, Symptoms of Overexposure

The severity of toxicological effects is dependent on the exposure concentration and exposure duration. The mode of action by which Vikane produces its toxicity in humans depends on the exposure concentration. In general, the effects of overexposure to high concentrations are central nervous system depression and respiratory irritation followed by pulmonary edema, which is the accumulation of fluids in the lungs and can result in death. Humans exposed to high concentrations of Vikane may expect to experience symptoms similar to drunkenness. Speech and movements may be slowed, and fingers, hands, and toes may become

Animal studies may indicate that some sulfuryl fluoride is converted to fluoride ion in the body. Chronic exposure may result in fluoride binding to the teeth and bones, causing fluorosis, which is manifested as mottled teeth.

Applicators who work with Vikane can have their urine checked for fluoride. However, high fluoride levels in the urine could be due to chemicals other than sulfuryl fluoride, for example, fluorides in drinking water, fluorinated tooth paste, and some medicines.

### Time to Incapacitation

Another factor to be considered in the safe use of Vikane is the length of time in which a person might have "escape capability" during exposure to high levels of Vikane. Researchers have investigated this by determining the length of time that rats are able to maintain coordinated activity when exposed to very high concentrations of Vikane. The time to incapacitation of laboratory rats for various exposure concentrations were (Nitschke et al. 1986):

42 minutes at 4,000 ppm 16 minutes at 10,000 ppm 10 minutes at 20,000 ppm 6 minutes at 40,000 ppm

Exposures were terminated when incapacitation occurred. All rats died or were moribund within 3 hours following the end of exposure. Therefore, the above exposures can be considered to produce 100% mortality in rats. For comparison, typical initial concentrations in single family homes are 1440-3850 ppm and must be reduced to 5 ppm or less before humans can enter dwellings without respiratory protection.

Manufactured by Interscan Corporation, Chatsworth, CA 91311
Manufactured by The Foxboro Company, East Bridgewater, MA 02333
See the section on FORMULATION AND PROPERTIES
See the section on EFFICACY
See the section on Vikane FUMIGANT DOSAGE DETERMINATION

#### Repeated Exposure Toxicity Studies

Rats, rabbits, and dogs have been studied following daily repeated exposures to Vikane. Exposures of 30 ppm 6 hours/day, 5 days/week for 13 weeks had no effects on rats or rabbits, while dogs showed no effects from 100 ppm in a simllar exposure regimen. Rats exposed to 300 ppm had decreased body weights, mottled teeth, and microscopic evidence of brain and kidney injury and respiratory irritation. Rabbits exposed to 100 or 300 ppm showed decreased body weights and microscopic changes in brain and nasal tissues. Dogs exposed to 200 ppm showed nervous system effects, including microscopic changes in the brain.

# Studies For Effects On Reproduction And Development Of Offspring

The results of the studies described here indicate that Vikane is not likely to have any effects on reproduction or development of offspring. Groups of pregnant rats and rabbits were exposed to Vikane at three different concentrations: 25, 75, or 225 ppm for 6 hours/day during the majority of the gestation period. Although the highest level of 225 ppm was toxic to the maternal animals (as would be expected), there was no evidence that Vikane was teratogenic (causing birth defects in offspring of exposed females). The only effects on the fetus were ... reduced body weights in the rabbits at the highest level, probably associated with the maternal weight loss. In a reproduction study, male and female rats were exposed to concentrations of 5, 20, or 150 ppm throughout two generations.

The highest level of 150 ppm was toxic to the parent animals, producing effects similar to those seen in the 13-week study described in the preceding section. Parent animals exposed to 5 ppm were without evidence of effects. Decreased weights of the offspring were observed at 150 ppm that may have been secondary to decreased maternal growth. The only effect observed at 20 ppm was mild lung irritation in parental rats, with no evidence of toxicity in offspring. There were no effects on reproductive performance in any exposure group.

#### Carcinogenicity And Mutagenicity Studies

Vikane has been tested in a battery of mutagenicity tests that serve as a screen for identifying chemicals that affect genetic mechanisms. All test results have been negative, indicating that Vikane is not mutagenic in standard testing. Lifetime studies in which rats and mice were exposed to Vikane to assess whether or not the chemical has potential to cause cancer were also negative.

#### Neurological Effects

Rats exposed for 6 hours a day for 2 days to 100 ppm and 300 ppm showed no signs of neurotoxicity.

#### Other Routes Of Exposure To Vikane

Inhalation is the primary route of exposure to Vikane. Ingestion is highly unlikely since the material is a gas at temperatures higher than -67°F. Laboratory animals maintained for 66 days on feed directly fumigated at 2 lb/1000 cubic ft. (7700 ppm) showed no adverse effects: Typical structural fumigation concentrations are 1/lb/1000 cubic ft (3850 ppm), or less. Feed exposed to abnormally high application rates (10-200 lb/1000 cubic ft; 38,500 to 770,000 ppm) and fed to test animals caused decreased body weight gains and fluorosis of the teeth. The gas is not absorbed through the skin in acutely toxic amounts; rats exposed dermally for 4 hours to concentrations of 9599 ppm did not show evidence of toxicity.

#### REFERENCES

Bailey, R. 1992. Sulfluryl fluoride: Fate in the atmosphere. Dow Chemical Company DECO-ES Report 2511. Midland, Michigan.

Derrick, M. R., H. D. Burgess, M. T. Baker, and N. E. Binnie. 1990 Sulfuryl fluoride (Vikane\*): A review of its use as a fumigant. JAIC 29: 77-90.

DowElanco! 1992. Fumigation manual for Vikane gas fumigant. DowElanco Indianapolis, Indiana.

Kenaga, E. E. 1957. Some biological, chemical, and physical properties of sulfury. fluoride as an insecticidal fumigant. J. Econ. Entomol. 50: 1-6:

Meikle, R. W., D. Stewart, and O. A. Globus. 1963. Drywood termite metabolism of Vikane gas fumigant as shown by labeled pool technique. J. Agric. Food Chem. 11 226-230

Meikle, R. W. and D. Stewart. 1962. Structural furnigants, the residue potential of sulfuryl fluoride, methyl bromide, and methane-sulfonyl fluoride in structural fumigations, J. Ag. and Food Chem. 12: 464-467.

Moon, B. L. 1981. Vikane gas helps save the Taj Mahal of North America. Ind. Veg. Pest Management, 13(1): 12-15.

National Research Council. Drinking Water and Health, 1977. National Academy of Sciences, Washington, D.C.

Nitschke, K. D., R. R. Albee, J. L. Mattsson, and R. R. Miller, 1986. Incapacitation and treatment of rats exposed to a lethal dose of sulfuryl fluoride. Fund, and Appl. Tox. 7: 664-670.

Outram, I. 1970. Some effects of the fumigant sulphuryl fluoride on the gross metabolism of insect eggs, Fluoride 3: 85-91

Osbrink, W. L. A., R. H. Scheffrahn, N.-Y. Su, and M. K. Rust, 1987. Laboratory comparisons of sulfuryl fluoride toxicity and mean time of mortality among ten termite species (Isoptera: Hodotermitidae, Kalotermitidae, Phinotermitidae). J. Econ. Entomol. 80: 1044-1047,

Pest Control, 1977. Dewey defends Hearst Castle against lyctus beetles, Pest Control 45(6); 30, 31, 48.

Scheffrahn, R. H., R.-C. Hsu, and N.-Y. Su. 1990. Evaluation of polymer film enclosures as protective barriers for commodities from exposure to structural fumigants. J Agric. Food Chem. 38: 904-908.

Stewart, D. 1957. Sulfuryl fluoride - A new furnigant for control of the Drywood termite Kalotermes minor Hagen. J. Econ. Entomol. 50: 7-11.

Su, N.-Y. and R. H. Scheffrahn. 1990. Efficacy of sulfuryl fluoride against four beetle pests of museums (Coleoptera: Dermestidae, Anobiidae). J. Econ. Entomol. 83: 879

> Dow AgroSciences LLC 9330 Zionsville Road Indianapolis, IN 46268

- The information herein is presented in good faith, but no warranty, express or implied, is given nor is freedom from any patent owned by Dow AgroSciences LLC or by others to be inferred.

\*DowElanco is now known as Dow AgroSciences LLC.